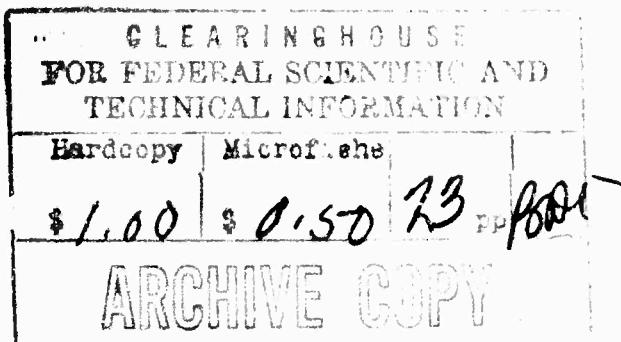


AD630459

ADVANCED RESEARCH PROJECTS AGENCY
Contract SD-88

Technical report No. ARPA-20

INTERSTITIAL DIFFUSION OF COPPER
AND SILVER IN LEAD

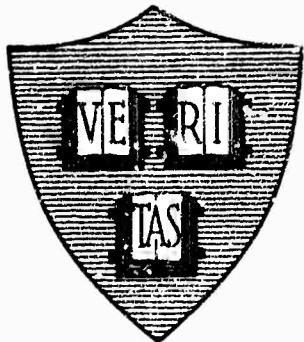


Code 1

By

B. F. Dyson, T. Anthony, and D. Turnbull

December, 1965



DIVISION OF ENGINEERING AND APPLIED PHYSICS
HARVARD UNIVERSITY • CAMBRIDGE, MASSACHUSETTS

INTERSTITIAL DIFFUSION OF COPPER AND SILVER IN LEAD

by

B. F. Dyson, T. Anthony, and D. Turnbull

Technical Report No. ARPA-20

Contract SD-88

December 1965

Submitted to:

Advanced Research Projects Agency

The Department of Defense

Division of Engineering and Applied Physics

Harvard University

Cambridge, Massachusetts

ABSTRACT

The diffusivities, D , of copper and silver in high purity lead have been measured by a radioactive tracer technique. They are described by:

$$D_{\text{Cu}/\text{Pb}} = 7.9 \times 10^{-3} e^{-\frac{8,020}{RT}} \text{ cm}^2 \text{ sec}^{-1}, D_{\text{Ag}/\text{Pb}} = 4.6 \times 10^{-2} e^{-\frac{14,440}{RT}}$$

$\text{cm}^2 \text{ sec}^{-1}$. These results, in combination with those of Seith and Keil and Ascoli et al., show that the rates of diffusion of the noble metals in lead are several orders of magnitude greater than the self diffusion rate of lead,

D_{Pb} . We have found that D_{Pb} is not measurably affected by the dissolution of either gold, in agreement with Seith and Keil, or of copper. The results indicate that neither the vacancy, interstitialcy nor exchange mechanisms are predominant in the diffusion of these solutes. It is concluded that the noble metals are dissolved in lead at least partially in the interstitial state and that they diffuse almost wholly by an interstitial mechanism.

INTERSTITIAL DIFFUSION OF COPPER AND SILVER IN LEAD

by

B. F. Dyson, T. Anthony and D. Turnbull

Division of Engineering and Applied Physics,
Harvard University, Cambridge, Massachusetts

INTRODUCTION*

Seith and Keil [1] measured the diffusion of gold and silver in lead using dilute and non-radioactive alloy couples. Their results are described by the equations:

$$D_{\text{Au}/\text{Pb}} = 1.03 \times 10^{-1} e^{-\frac{14,700}{RT}} \text{ cm}^2 \text{ sec}^{-1}$$

and

$$D_{\text{Ag}/\text{Pb}} = 7.45 \times 10^{-2} e^{-\frac{15,200}{RT}} \text{ cm}^2 \text{ sec}^{-1}.$$

Later, Ascoli et al. [2,3] measured the diffusion of radioactive gold in lead. Their results are in substantial agreement with those of Seith and Keil at high temperatures but were found to be best described over the wider temperature range by the equation:

$$D_{\text{Au}/\text{Pb}} = 4.1 \times 10^{-3} e^{-\frac{9,350}{RT}} \text{ cm}^2 \text{ sec}^{-1}.$$

The disagreement between the studies at low temperatures is probably due to uncertainties in the Seith and Keil work resulting from the low solubility of gold in lead.

* This work was presented at the American Physical Society Meeting, Chicago, Illinois in October 1965.

A striking feature of these results is their indication that the diffusion rate of these impurities in lead is many orders of magnitude greater than the self diffusion rate of the pure solvent metal which is described by: [4]

$$D_{Pb/Pb} = 4.6 \times 10^{-1} e^{-\frac{24,800}{RT}} \text{ cm}^2 \text{ sec}^{-1}$$

The findings of Ascoli et al., that the diffusion rates of gold in single and in polycrystalline lead samples are equal, indicates that the results were not appreciably affected by grain boundary short circuiting.

Seith and Keil recognized that the self-diffusion rate of lead should be strongly enhanced by small additions of gold or silver if these impurities diffused by an interchange mechanism. In particular, they calculated that with the addition of 0.03 atom % gold, the self-diffusion rate of lead should be increased by a factor of 116 at 200°C and by a factor of 40 at 243°C. Actually they found no measurable effect of gold additions on the rate of self-diffusion of lead. The negative results of these experiments seems to rule out not only the interchange mechanism but also the vacancy and interstitial mechanisms for the predominant mechanism of diffusion of gold in lead. This leaves the interstitial mechanism as the most likely one and this was the conclusion of Seith and Keil.

Predominantly interstitial solutions of one metal in another are unusual and there is rather little information on their properties. Therefore, we decided to investigate further the diffusion behavior of the noble metals in lead. This paper reports new results on the rate of diffusion of copper in lead and on the effect of dissolved copper on the rate of self-diffusion of lead. Also we

report additional measurements to check the results of Seith and Keil on the diffusion of silver in lead and on the effect of dissolved gold on the self-diffusion of lead.

EXPERIMENTAL PROCEDURE

(a) Copper

Single and polycrystalline specimens in cylindrical form (3/4" diameter and 6" long) were prepared from zone refined lead (Cecinco 69). The cylinders were sectioned into 3/4" lengths using a Servomet spark machine with a tantalum wire cutter. Because of the high grain boundary mobility in lead of this purity, the polycrystalline specimens contained only two or three grains per section. After sectioning, each specimen was etched in dilute nitric acid and then one face was planed flat using a horizontal microtome. The sections were then sealed in an evacuated capsule and annealed at approximately 325°C for four hours and furnace cooled.

Radioactive copper 64 (Specific Activity 1 Curie/gm.) was chemically deposited onto the microtomed surface. We found that unless special care was taken in this process a major part of the deposited isotope was "trapped," presumably by an oxide film, at the surface and did not enter the specimen during the diffusion anneal. This phenomenon is discussed more fully in the Appendix. However, the formation of oxide was minimized, so that all the deposited isotope diffused into the specimen, with the following procedure which was used in all the experiments reported here. The specimen was cleaned in acetone, etched slightly in dilute nitric acid and quickly transferred to an adjacent acidified radio-copper acetate solution. After 1-2 minutes, the specimen

was removed from this solution and quickly rinsed in alcohol and then acetone, and blotted dry. The specimen was then transferred to a stainless steel capsule which was evacuated to 10^{-5} torr and partially back filled with high purity neon or helium. The sealed capsule was then placed in a preheated furnace containing a large hollow cylindrical copper insert having an inside diameter equal to the outside diameter of the capsule. A chromel-alumel thermocouple was inserted into a hole in the capsule and the furnace closed at each end with insulating brick which was butted against the copper insert. The heating curve was recorded in order to obtain a corrected diffusion time since the annealing times were only from 1 - 3 hours. The furnace temperature was stabilized to $\pm 1/2^{\circ}\text{C}$ by means of a thermocouple located on the furnace windings and connected to a West J. P. controller. The measuring thermocouple was checked against a standardized Pt - Pt/Rh couple. After the appropriate annealing time the capsule was quenched into water and the sample reduced to a diameter of 0.35" on a lathe. It was then transferred to the microtome and the active face leveled with the plane of motion of the blade by means of a mechanical dial indicator which could be read to 1 μ . Since the indicator ball would damage the lead surface, an optically ground glass disc was placed on top of the specimen. The microtome was set to cut 10 μ slices which were collected into groups of 10 for weighing and counting. The weighings were made on a Mettler semi-micro balance and counted with a thin end-window flow Geiger counter with standardized geometry. The actual slice thickness was calculated from the mass of each group of slices and the known density of 11.35 gm/cc. A total of 50 data points were obtained for each specimen which corresponded to a total penetration of approximately 5,000 μ .

(b) Silver

Rectangular single crystals of lead (8" x 1/2" x 1/4") were grown from Cominco 69 stock. These were cut on the spark machine into 1/2" x 1/2" x 1/4" samples. The preparation of the samples up to the deposition of the silver was essentially as described for the copper. Radioactive silver 110 (specific activities of 50 Mc/gm and 1 C/gm were used) was either electroplated from a cyanide solution or chemi-deposited from an acidified nitrate solution. The annealing was performed either in air or in evacuated stainless steel capsules. The annealing time (t) was such as to give a $(Dt)^{1/2}$ (where D is the approximate diffusion coefficient) value of approximately 200μ and a total of 25 data points were obtained per specimen. The activity was measured with a well type single channel gamma spectrometer.

RESULTS

The solute concentration for both silver and copper was found to obey a gaussian distribution* and so the diffusion coefficients were determined from the slope of a plot of logarithm of concentration vs. the square of the penetration. Figures 1 and 2 show the logarithm of the diffusivities of copper and silver plotted against the reciprocal of the absolute temperature. Note that the copper diffusivities obtained with polycrystalline samples are in accord with those found with single crystals. The diffusivities obey an Arrhenius

*See Appendix

type relationship and so activation energies (Q) and pre-exponential factors (D_0) were calculated by the method of least squares. The results are shown in Table I. The values of D_0 and Q for silver are essentially in agreement with those of Seith. [1]

The diffusivities of the noble metals in lead and that of the lead self diffusivity are compared in Fig. 3. The curves for gold and lead are drawn from the data of Ascoli [3] (Au) and Hudson and Hoffman [4] (Pb). At the melting point of lead, $D_{\text{Cu}}/D_{\text{Pb}} = 2 \times 10^4$ and $D_{\text{Au}}/D_{\text{Pb}} = 4 \times 10^3$. This means that if copper and gold are diffusing by a vacancy mechanism, the tracer diffusivity of lead should be greatly enhanced by addition of even small amounts of either of these solutes to the lead, particularly copper.

The enhancement can be shown to be given by: [5]

$$D_{\text{Pb}}/D_{\text{Pb}}^0 = 1 + \beta X_s D_s/D_{\text{Pb}}^0 \quad \text{----- (1)}$$

D_{Pb} = lead diffusivity in the alloy.

X_s = mole fraction of solute in alloy.

D_s = solute diffusion coefficient.

D_{Pb}^0 = lead self diffusion coefficient in pure lead.

β = number of vacancy - solvent exchanges that occur in the region around a solute atom while the latter is completing a diffusive step.

The lower limiting value of β should be unity while the upper limiting value may be of the order of the coordination number.

To determine whether such an enhancement occurred. Pb - 0.02 at. % Cu and Pb - 0.02 at. % Au single crystals were prepared. Small alloy contents had to be used because of the restricted solid solubility in these systems (~ 0.024 at. % Copper at 326°C and 0.08 at. % gold at 200°C). Radioactive Pb^{210} was electroplated onto the the surface of the alloys which were then annealed for approximately 15 days at 223°C. The specimens were then sectioned with the microtome into 5 μ slices. The Bi^{10} β ray was counted after waiting 30 days for secular equilibrium to occur between Pb^{210} and Bi^{210} . The results are shown in Table II together with the theoretical values of D_{Pb}/D_{Pb}^0 calculated with $\beta = 1$ which therefore make them minimum values. The value for D_{Pb}^0 was calculated from Hudson and Hoffman's results. Since the solubility of copper in lead is not accurately known, the theoretical value of D_{Pb}/D_{Pb}^0 was calculated using the minimum value of 0.005 at. % copper found in our diffusion experiments. The self diffusion of lead is seen to be unaffected by alloying which is contrary to the large effects predicted on the assumption of a vacancy mechanism.

DISCUSSION

Our findings and the earlier ones of Seith and Keil that the self-diffusion coefficient of lead is unaffected by dissolution of the noble metals (Cu, Ag and Au) indicate that neither the vacancy, interchange nor interstitialcy mechanisms can be predominant in the diffusion of noble metals in lead. This leaves the possibilities that the diffusion is effected either by an interstitial mechanism or by grain boundary or dislocation short circuiting.

The absence of measurable grain size effects on diffusion in the experiments of Ascoli et al. [2, 3] ($\text{Au} \rightarrow \text{Pb}$) and in our experiments ($\text{Cu} \rightarrow \text{Pb}$) apparently rules out appreciable grain boundary short-circuiting. Also it seems unlikely that dislocation short-circuiting plays a major role in the diffusion. The reasons are: (1) the logarithm of the isotope concentration, following a diffusion anneal, decreases as the square of the penetration depth; (2) at large penetrations the amounts of diffused solute were many orders of magnitude more than required to completely coat the dislocation lines with solute. For example, at a penetration of $3(Dt)^{1/2}$ the number of diffused copper atoms in a 1 cm^2 section one atom high was estimated to be greater than 10^9 which is to be compared with the 10^6 or so dislocation cores expected in the same well annealed section. Similar conclusions can be drawn from the experiments of Seith and Keil.

Therefore we conclude that the interstitial mechanism is probably the predominant one for the diffusion of the noble metals in lead. The formal description of the diffusive process should then be the same as that which was developed for the diffusion of copper in germanium: [6] thus:

$$D = D_i \frac{C_i}{C_s + C_i} = D_i X_i$$

where D = the observed diffusion coefficient

D_i = the diffusior coefficient of the solute when in the interstitial state

C_i = the concentration of solute in the interstitial state

C_s = the concentration of solute in the substitutional state,

and where the contribution of the vacancy mechanism to the diffusion has been neglected.

Note that the observed diffusion coefficient is the product of two factors: the diffusion coefficient of the interstitial atom and the fraction, X_i , of the solute atoms in the interstitial state. In most metallic solutions X_i is presumed to be negligible, perhaps $X_i < 10^{-10}$. By contrast the fraction of noble metal atoms in interstitial positions in lead should be of the order of 10^{-4} at least, and possibly near unity for copper, to account for the diffusion results.

It is surprising that the proportion of metal atoms in interstitial positions is so large in these alloys. Comparing these systems with the system copper in germanium it might seem that the tendency of the noble metals to dissolve interstitially is directly connected with the grouping of the solvent in the periodic table. However, the interstitial behavior of copper in germanium presumably is favored by the relatively open germanium structure. On the other hand, the sizes of the interstitial positions in face-centered cubic lead, calculated from the atomic radius (1.75\AA) of lead, are much too small to accommodate noble metal atoms (atomic radii, Cu: 1.25\AA , Ag: 1.4\AA Au: 1.4\AA) if the atoms must pack as hard spheres. However, it may be possible to account for the tendency toward interstitial formation in these systems if the packing is limited by ion rather than by atom size. For example, the radii of octahedral holes bounded by the ion cores of lead would be 1.28\AA and 1.62\AA for doubly and quadruply ionized lead, respectively.

The corresponding numbers for tetrahedral holes are 0.94\AA and 1.29\AA .

Therefore, it appears that noble metal atoms could be placed at least in octahedral holes with little or no distortion.

These ideas will be further developed and applied to the interpretation of the diffusion behavior of the noble metals in lead in a later paper.

ACKNOWLEDGMENTS

This work was supported in part by the Advanced Research Projects Agency under Contract ARPA-SD-88, and by the Division of Engineering and Applied Physics, Harvard University. One of the authors (T. Anthony) was supported by a National Science Foundation Graduate Fellowship.

REFERENCES

1. W. Seith and A. Keil, *Physik Chemie B* 22 350, 1933.
2. A. Ascoli, E. Germagnoli and L. Mongin, *Nuovo Cimento* 4, 123, 1956.
3. A. Ascoli, *J. Inst. Met.* 89, 218, 1961.
4. J. B. Hudson and R. E. Hoffman, *Trans. A.I.M.E.* 221, 761, 1961.
5. R. E. Hoffman, D. Turnbull and E. W. Hart, *ACTA Met.* 3, 417, 1955.
6. F. C. Frank and D. Turnbull, *Phys. R. v.* 104, 617, 1956.

APPENDIX

In some of our early experiments the specimens exhibited non-gaussian penetration behavior after the diffusion anneal. The characteristics of this were an initial rapid decrease in isotope concentration with distance followed by apparent gaussian behavior (See Fig. 4). The magnitude of the initial fall-off increased with decreasing annealing temperature. Diffusion coefficients calculated from the gaussian part of these curves were lower than those calculated from experiments in which the initial fall-off was eliminated. Ascoli et al., [2] also observed the initial fall-off in some experiments and attributed it to grain boundary short-circuiting. However, this would lead to an anomalously high concentration of isotope at large rather than small penetrations.

We have established that the initial rapid fall-off does not occur and that the concentration is gaussian at all penetrations when sufficient precautions are taken to minimize the thickness of the oxide film at the lead surface prior to the deposition of the isotope. This was achieved with the techniques already described for all the results reported here. We conclude that the anomalously high initial decrease in concentration, when it did occur, is due to the high resistance to isotope transport of the oxide film interposed between most of the isotope and the specimen. We now show that the observations are consistent with this conclusion.

When appreciable oxide is present in the deposition process, a part of the isotope will be in contact with the metal surface and "free" to diffuse at the beginning of the anneal while another part will be trapped at the outer surface of the oxide film. If the oxide film is quite thick, it may be that no appreciable part of the "trapped" isotope will reach the metal surface - the

diffusion anneal. In this case, only the gaussian penetration of the free isotope will be observed. Indeed we found that when the diffusion anneal was carried out in air, only a small fraction of the isotope had penetrated into the metal specimen; however, its penetration was entirely gaussian and described by values of the diffusion coefficient in excellent agreement with those obtained when no significant hold-up due to oxide was observed (i.e., all the deposited isotope exhibited a gaussian distribution at the end of the diffusion anneal). It is presumed that in the air anneal the oxide film was so thick that no significant amount of trapped isotope reached the specimen.

When the oxide film is thinner, appreciable amounts of the "trapped" solute may reach the oxide-metal interface during the diffusion anneal and especially at its later stages. This will result in the high and rapidly falling concentration of isotope in the vicinity of the metal surface observed in some specimens after the diffusion anneal. Under these conditions, the amount of originally trapped solute which actually diffuses into the lead will increase markedly with temperature since the activation energy is probably much larger for the oxide than for the metal diffusion. In agreement with this, the initial amount of fall-off to the gaussian curve did decrease with increasing temperature in those experiments where there was an appreciable thickness of oxide film.

These oxide film effects can be very prominent in studies on the diffusion of noble metals into lead because lead is easily oxidized and the diffusivities of the metals are probably orders of magnitude higher in lead than in the oxide. However, it is possible that these effects may have been operative in some of the other diffusion investigations in which anomalously high fall-offs in solute concentration were found in thin layers at the specimen surface.

TABLE I

Solute	D_o $\text{cm}^2 \text{ sec}^{-1}$	Q cal. mole^{-1}
Copper	$7.9 \pm 2.0 \times 10^{-3}$	$8,020 \pm 400$
Silver	$4.6 \pm 1.0 \times 10^{-2}$	$14,440 \pm 500$

Table I. Summary of constants D_o and Q ($D = D_o e^{-\frac{Q}{RT}}$) obtained in this investigation for the diffusion of copper and of silver into lead.

TABLE II

Solute	D_{Pb}^0 $\text{cm}^2 \text{ sec}^{-1}$	D_{Solute} $\text{cm}^2 \text{ sec}^{-1}$	D_{Pb} $\text{cm}^2 \text{ sec}^{-1}$ (Exp)	D_{Pb}/D_{Pb}^0 (Exp)	D_{Pb}/D_{Pb}^0 Eqn. 1
Cu	5.8×10^{-12}	2×10^{-6}	5.20×10^{-12}	~ 1	> 15
Cu	5.8×10^{-12}	2×10^{-6}	5.63×10^{-12}	~ 1	> 15
Au	5.8×10^{-12}	3×10^{-7}	5.39×10^{-12}	~ 1	11

Table II. Summary of results on the effect of the dissolution of copper and gold on the self-diffusion coefficient of lead at 223°C .

D_{Pb}^0 is the self-diffusion coefficient of pure lead and D_{Pb} is the self-diffusion coefficient of lead with an admixture of 0.02 atom % of solute. If all the added copper was dissolved, the calculated D_{Pb}/D_{Pb}^0 for the copper impurity would be 60 (in place of > 15) for the vacancy mechanism.

FIGURE CAPTIONS

Fig. 1: Diffusivity of copper in lead.

Fig. 2: Diffusivity of silver in lead.

Fig. 3. Comparison of the diffusivities of copper, gold, silver and lead in lead.

Fig. 4: A is a representative penetration curve for the diffusion of copper into lead at 224°C under conditions which minimized surface oxide formation in the isotope deposition and diffusion processes.

B is a penetration curve (copper into lead at 256°C) obtained in an experiment in which due care was not taken to minimize oxide formation during the isotope deposition. It shows the rapid initial fall-off in concentration followed by gaussian penetration.

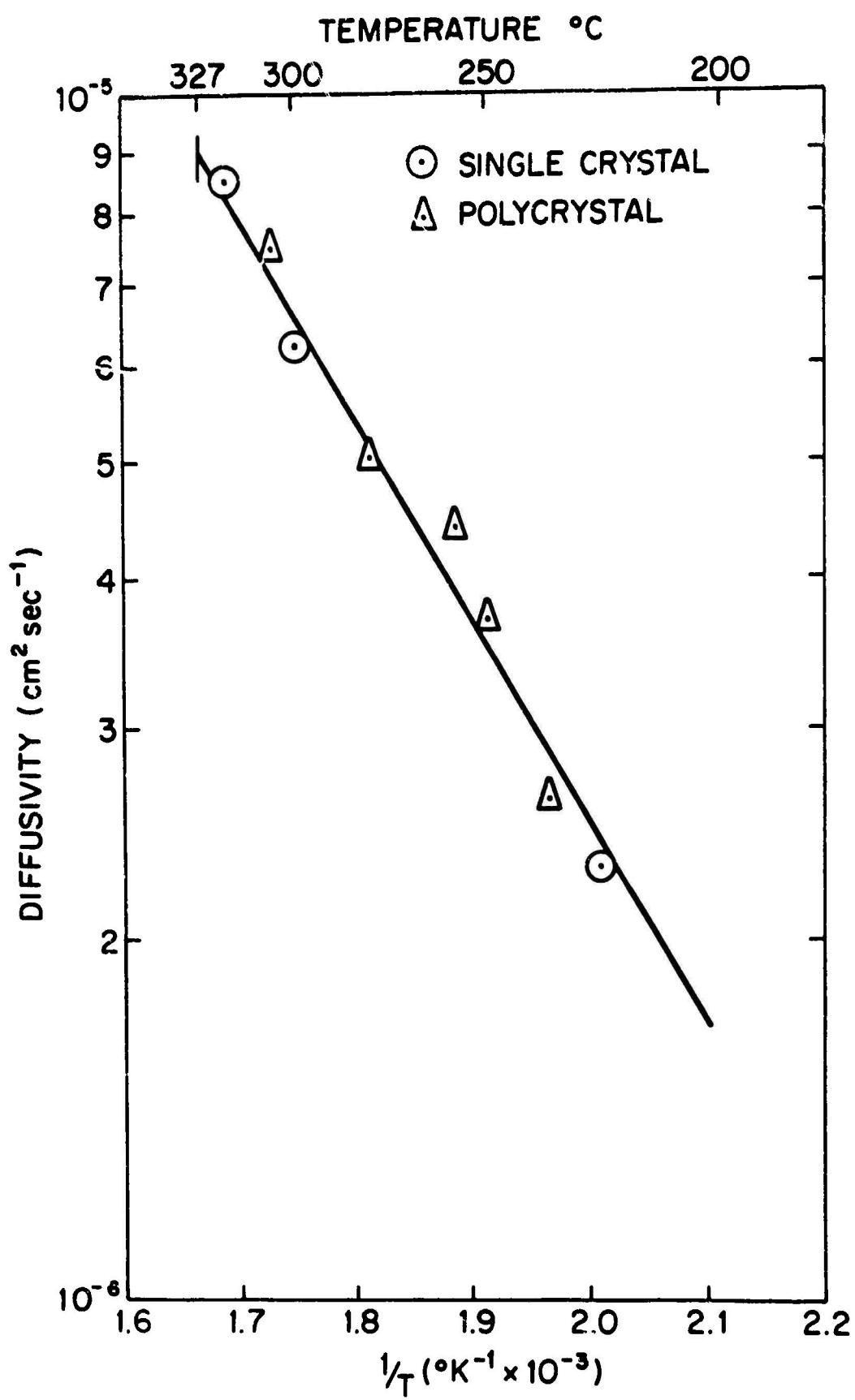


FIGURE 1

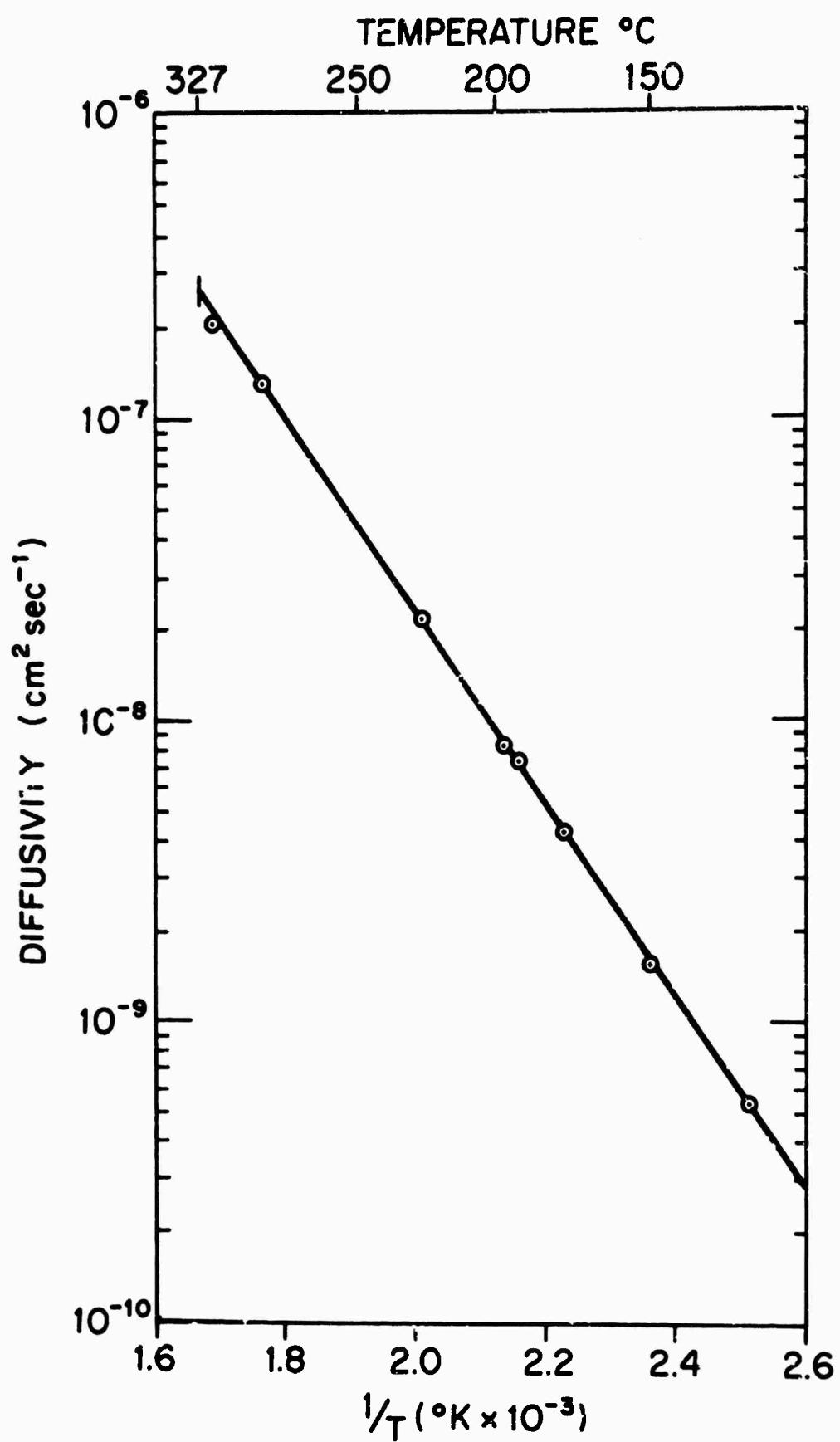


FIGURE 2

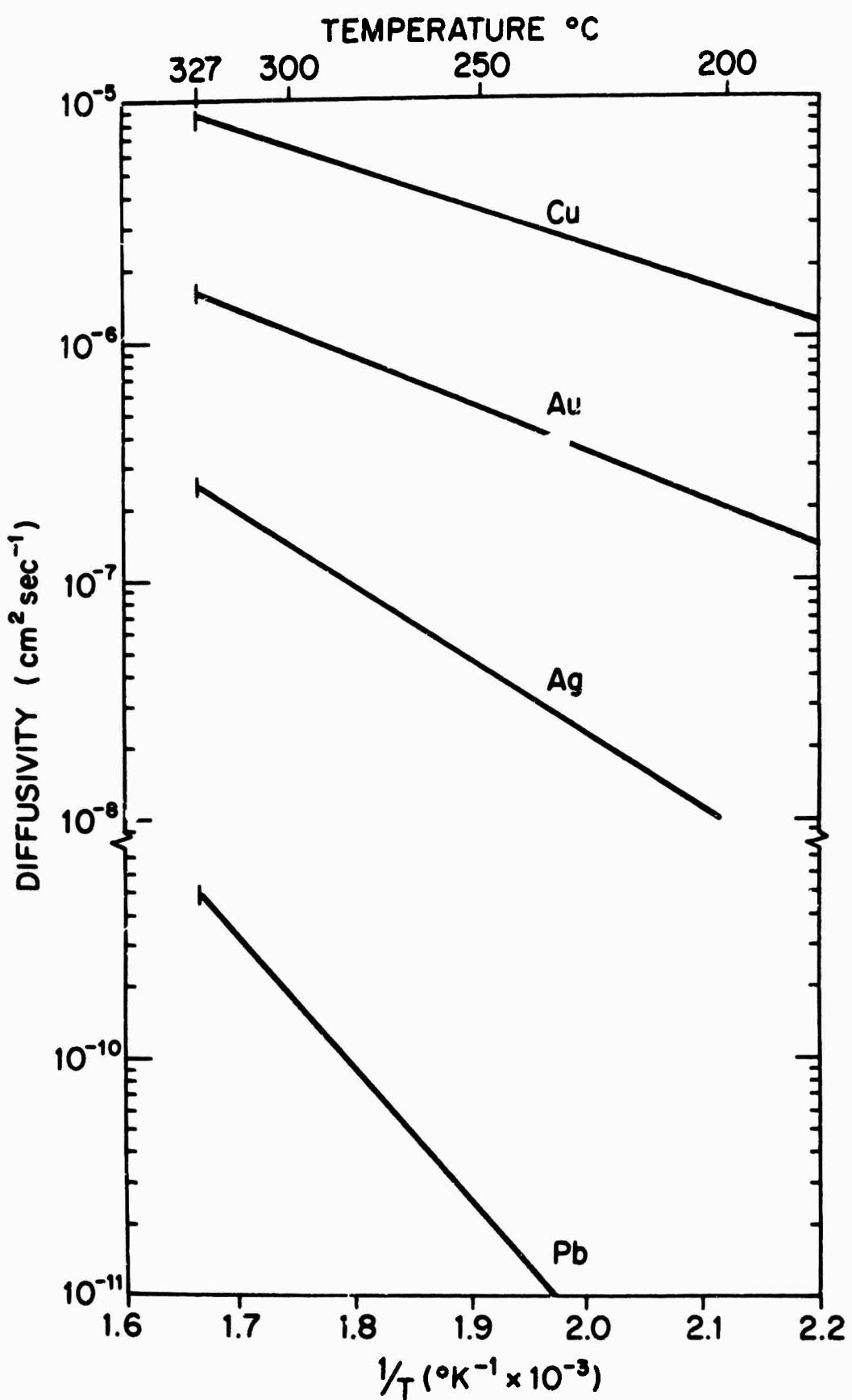


FIGURE 3

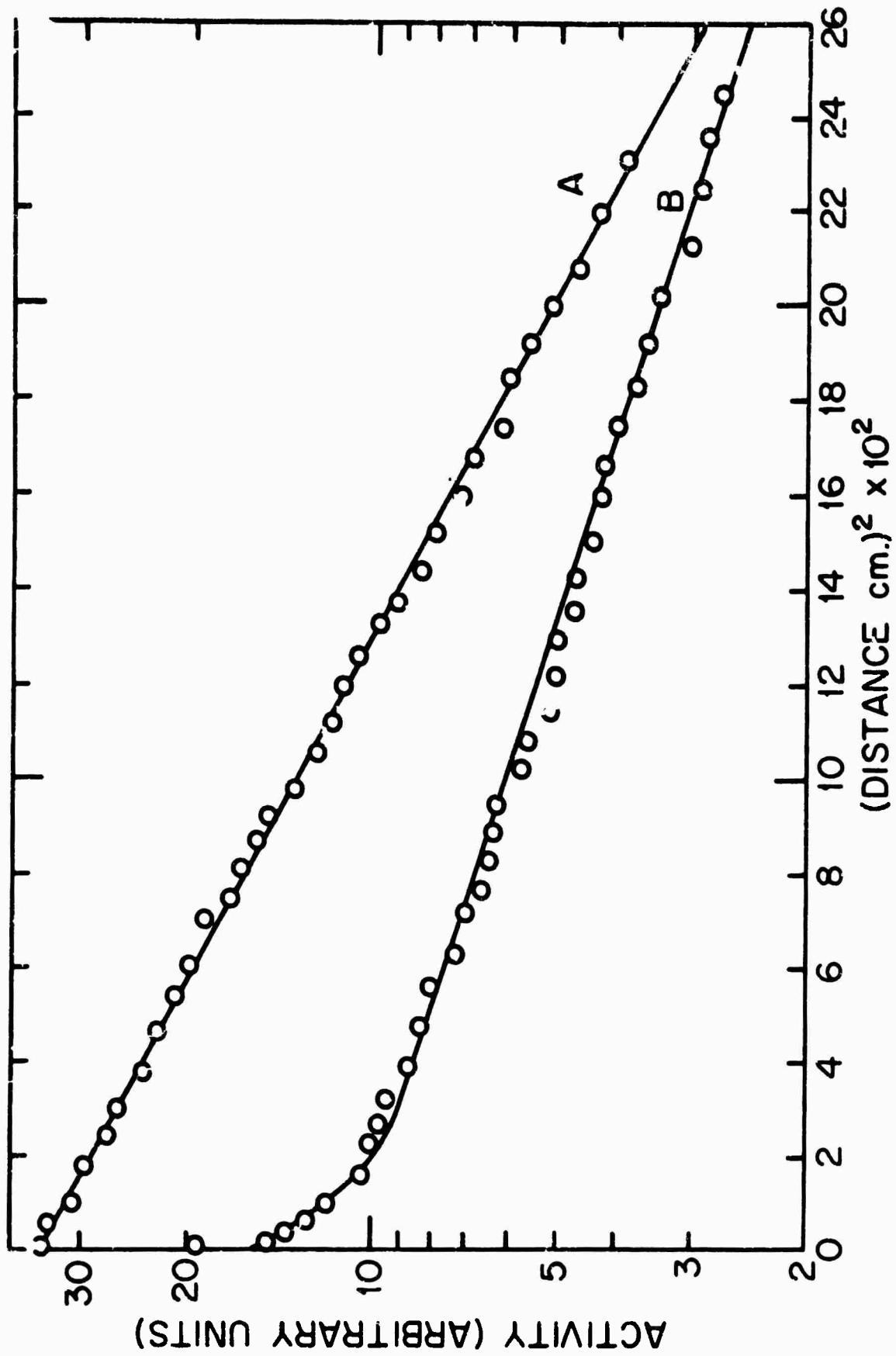


FIGURE 4